BIOCHAR FROM BAMBOO AS ADSORBENT FOR REMOVAL OF REACTIVE ORANGE 16

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DECLARATION

I hereby declare that the work embodied in this Report is the result of the original research except for the quotations and citations which have been duly acknowledged.

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LIST OF SYMBOL

°C	Degree Celcius
%	Percent q_{max} Langmuir monolayer
$\bar{x}$	Mean
μm	Micrometer
Ce	Equilibrium concentration of RO16, mg/L
C_o	Initial concentration of MG dye, mg/L
G	Gram
K_F	Freundlich multilayer adsorption capacity, mg/g
K_L	Langmuir equilibrium constant of adsorption, L/mg
L	Litre
mL	Mililitre

adsorption capacity, mg/g **LIST OF ABBREVIATIONS**

BB	Biochar Bamboo
et al.	And other
RO16	Reactive Orange 16
SD	Standard deviation
t_6	t-test value obtained from statistical table
t_{calc}	Calculated t-test value

Arang Bio Daripada Buluh Sebagai Bahan Penjerap Bagi Penyingkiran Pewarna Reaktif Jingga 16

ABSTRAK

Lambakan sisa buluh mempunyai potensi sebagai bahan penjerap kos rendah bagi rawatan buangan air. Kajian ini membentangkan potensi arang daripada buluh sebagai penjerap bagi penyingkiran pewarna Reaktif Jingga 16 (RO16). Terdapat beberapa parameter telah dikaji seperti kesan suhu pengkarbonan, dos bahan penjerap, kepekatan awal pewarna, masa sentuhan dan pH. Keputusan menunjukkan nilai optimum yang diperolehi pada suhu pengkarbonan 800 °C, dos penjerap 2 g, kepekatan awal pewarna 100 mg/L, masa sentuhan 12 jam dan pH 6. Peratusan tertinggi bagi penyingkiran pewarna RO16 dengan menggunakan arang buluh (BB) ialah 99.94 %. Data keseimbangan adalah paling sesuai dengan isoterma penjerapan Langmuir dengan kapasiti penjerapan maksimum adalah 4.859 mg/g dan $R^2 = 1$.

Kata Kunci: Penjerapan; Arang Buluh; Pewarna Reaktif Jingga 16; Model Langmuir

Biochar from Bamboo as Adsorbent For Removal of Reactive Orange 16

ABSTRACT

The abundant of bamboo waste has a potential as low cost adsorbent in waste water treatment. This study presents the potential of biochar from bamboo as adsorbent for removal of Reactive Orange 16 dye (RO16). There are several parameter have been studied such as effect of carbonization temperature, adsorbent dosage, initial concentration, contact time and pH. The results showed that the optimum value ware obtained at carbonization temperature of 800 ℃, adsorbent dosage of 2 g, intial concentration of 100 mg/L, contact time of 12 h and pH 6. The highest percentage for removal of RO16 dye using biochar bamboo (BB) was 99.94 %. The equilibrium data was best fitted on Langmuir adsorption isotherm with maximum adsorption capacity of 4.850 mg/g and $R^2 = 1$.

Keyword: Adsorption; Biohar Bamboo; Reactive Orange 16 Dye; Langmuir Model

CHAPTER 1

INTRODUCTION

1.1 Research Background

Dye was applied in variety of industrial sector for example textiles, cosmetic, pharmaceutical and food industry. However, either natural or synthetic dye has their side impact to human wellbeing and ecology. Some natural dye consist hematein and hematoxylin that cause irritation and inflammation when inhaled or ingested through skin (Paula, 2007). In 1856, William Henry Perkin discovered the first synthetic dye, mauveline. Synthetic dye including Reactive Orange 16 (RO16) dye can reduce water transparency, reduce solubility of gas also can induce carcinogenic and mutagenic (Gomes et al., 2011).

A few methods were found to reduce water pollution from untreated dye effluent that dumped directly on body of water. The methods used are ion exchange, coagulation, membrane separation, advanced oxidation, electrochemical destruction and adsorption. The utilization in industry of those methods are less because the colour removal are incomplete and need high energy and high operation cost (Shobana & hangam, 2012). Adsorption is process consist of two component involve adsorbate and adsorbent. Adsorbent is the substance contains the charge site on its surface while adsorbate is molecule being attach on charge site of adsorbent. There is another approach to evacuate the RO16 dye which is adsorption of this dye using biochar from bamboo waste. Charcoal is suitable for water filtration due to effective adsorption because it has abundant charged sites that can hold ions of elements and biomolecules. The optimum condition for removal of Reactive Orange 16 dye and the adsorption capacity of bamboo in form of biochar was investigated using a few parameters. The parameters involved are effect of carbonization temperature, adsorbent dosage, initial dye concentration, contact time and pH. The Langmuir and Freundlich adsorption isotherm was used to reveal the adsorption favourability.

1.2 Problem Statement

Nowadays, synthetic dye have high demand regarding it useful, faster and effectiveness in textile, cosmetics, food, paper and pharmaceutical industry compared to natural dye. However, some of synthetic dye is toxic and dangerous to human. Otherwise, the residual of dye always flow to the river, beach and drainage. It creates ecological problems and health hazards all over the world. It also causes the reduction on water transparency, oxygen solubility, and bad impact of plant growth (Govindwar et al., 2014).

1.3 Objectives

The objectives of this study are:

i. To investigate the potential of biochar based on bamboo for the removal of Reactive Orange 16 (RO16) dye.

ii. To determine the optimum parameters and suitable adsorption isotherm for the removal of Reactive Orange 16 dye using biochar based on bamboo as an adsorbent.

iii. To characterise the biochar based on bamboo using SEM and FTIR.

1.4 Scope of Study

In this study, bamboo waste that undergoes conversion process to become biochar was used as bioadsorbent. The bamboo waste was obtained from Pasir Gudang, Johor and Agro Park of University Malaysia Kelantan, Jeli. In this study, there are several adsorption parameters were examined to identify the ability of biochar as adsorbent for removal of Reactive Orange 16 dye which are effect of carbonization temperature, effect of adsorbent dosage, effect of initial dye concentration, effect of contact time and effect of pH. The characterisation of biochar bamboo was conducted using Scanning Electron Microscope (SEM) and Fourier Transforms Infrared Spectroscopy (FTIR).

1.5 Significance of Study

The investigation of this study is significant to solve the problem that faced by industry that using dye in their product. The technique that applied in this study is adsorption of Reactive Orange 16 dye using agriculture waste as adsorbent which is bamboo biochar. The treatment of dye removal was improved by using biochar. Biochar was used because it contains high carbon, high surface area and high level porosity that can attract more molecules of dye on biochar surface (Ma et al., 2001). By applying this technique in industry, it can reduce the cost for water treatment from dye pollution, sustainable the aquatic habitat, increase the water transparency.

CHAPTER 2

LITERATURE REVIEW

2.1 Utilisation of Agricultural waste as adsorbent

The concept of biorefinery making the utilisation of agriculture waste as value added in industry become increase. For example, jackfruit peel remove brilliant green dye, rambutan peel remove porcion red dye and sugarcane bagasse activated carbon remove acid blue dye (Mohd Nor et al., 2015). In this study, the agriculture waste that used as adsorbent is bamboo. To improve the efficiency of adsorbent, the bamboo was modified become biochar. The benefits of using bamboo biochar are not harmful to environment, safe cost and biodegradable.

2.1.1 Bamboo

Bamboo was shown at Figure 2.1 is belongs to subfamily which is Bambusoideae of the grass family Poaceae. The chemical compositions inside the bamboo are cellulose, hemicellulose, lignin and extractive. The bamboo stem consist of hollow and vascular bundles with parenchyma cells, free fiber strands and conducting tissue such as vessel and sieve tube. Bamboo can be as adsorption agents in industry by treatment become modify bamboo, biochar and activated carbon. The adsorption capacity usually have smaller value in biochar compare to activated carbon (Gomes et al., 2011) and have higher value compare to modify bamboo. Thus, the micropore size distribution in biochar is much narrower than in the activated carbon because the activated carbon conducted treatment to increase the efficiency in industry. Therefore, the bamboo as adsorbent with different adsorption capacity was shown in Table 2.1.

Table 2.1: Bamboo as adsorbent

Adsorbent	**Adsorbate**	**Adsorption Capacity Mg/g**	**Reference**
Modifying bamboo waste	Disperse 167	36.54	(Wang, 2013)
Modifying bamboo waste	Methylene blue	87.71	(Hameed & Tan., 2010)
Modifying bamboo sawdust	Direct red 81	13.83	(Khan et al., 2012)
Bamboo based activated carbon	Methylene blue	454.2	(Hameed et al., 2007)
Bamboo charcoal	Metylene blue Acid Orange 7	17.32 9.28	(Liao et al., 2012)
Bamboo charcoal	2,4-Dichlorophenol	45.25	(Ma et al., 2010)

Figure 2.1: Bamboo

2.1.2 Biochar from bamboo as adsorbent for Reactive Orang 16 dye

Biochar is defined as biomass that heated in a closed container with little or no available air to produce carbon-rich product (Lehmann J. and Joseph S., 2009). Pyrolysis and carbonization is a method used to produce biochar (Lehmann et al., 2011). High carbonization temperature contributes to high surface area toward biomass. The advantages of biochar application including improvements in plant growth and removal dye (Chan et al., 2007). Biochar that produced from bamboo was shown at Figure 2.2. It was chosen as adsorbent for removal of Reactive Orange 16 dye in aqueous solution. Slow carbonization generally occur at 400–800 °C in 1-4 h under Nitrogen (Mui et al., 2010). Biochar decrease as rising temperature because the partial gasification occurs toward lignin and hemicelluloses. High carbonization temperatures caused surface area and porous of char become high.

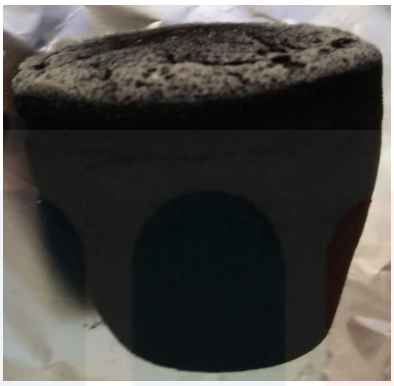


Figure 2.2: Biochar bamboo

2.1.3 Pyrolysis

Slow pyrolysis commonly used in biochar production due to the effectiveness on biochar application and can save environment (Jiang et al., 2015). From Table 2.2, the outcome of main product and by-product is different depend on type of pyrolysis used. The temperature between 200 ℃ and 500 ℃ is the major decomposition processes during pyrolysis (Chen & Chen, 2009; Shen et al., 2012). Decomposition process follows three phases which are from the half to complete decomposition. First decomposition occurs toward hemicellulose. Second decomposition occur toward cellulose and last toward lignin (Chen & Chen, 2009). Table 2.3 shows the different pyrolysis technique on different feedstock.

Table 2.2: Type of pyrolysis used and the operating parameter

Pyrolysis System	Product	By-Product	Temperature (℃)	Heating Rate (℃/s)
Slow pyrolysis	Biochar and biogas	Oil	300-550	0.01-2
Fast pyrolysis	Gas	Liquid and less biochar	>600	$>10_5$
Flash pyrolysis	Liquid	Gas and less biochar	400-600	10-1000

Source: Mandal et al., (2016)

Table 2.3: The different pyrolysis technique on different feedstock

Feedstocks temperature	Pyrolytic time	Residence techniques	Pyrolysis (C)	Contaminants	References
Bamboo	450, 600	–	Slow pyrolysis	Sulfamethoxazole	(Yao et al., 2012)
Eucalyptus	400	30 min	Slow pyrolysis	Methylene blue dye	(Sun, Wan, & Luo, 2013)
Hardwood	450	<5 s	Fast pyrolysis	Copper and Zinc	(Chen et al., 2011)
Rice husk	350	4 h	Slow pyrolysis	Pb, Cu, Zn, and Cd	(Xu, Cao, & Zhao, 2013)

2.2 Reactive Orange 16 (RO16)

In this study, Reactive Orange 16 was chosen as an adsorbate (Figure 2.3) while Figure 2.4 shows the chemical structure of Reactive Orange 16. The chemical formula for RO16 is $C_2OH_{17}N_3Na_2O_{11}S_3$. Reactive Orange16 has 617.54 g/mol molar mass and 494 nm for maximum wavelength (Won et al., 2006). Variety of adsorbent has been applied for the removal of reactive orange 16 has been reported in literature (Table 2.4).

Figure 2.3: Reactive Orange 16

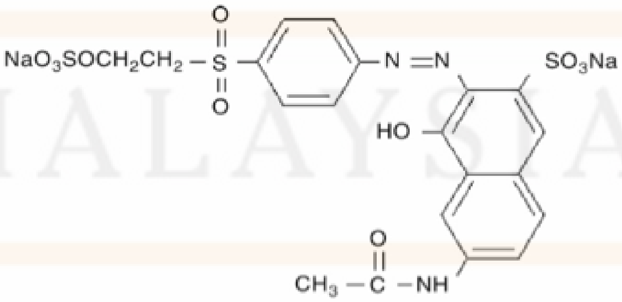


Figure 2.4: Chemical Structure of Reactive Orange 16

Source: Won et al., (2006)

Table 2.4: Variety of adsorbent that has been applied in removal of reactive orange 16

Adsorbent	Adsorption capacity, mg/g	Reference
Wood activated carbon	367.5	(Lee et al., 2006)
Coal activated carbon	326.4	(Lee et al., 2006)
Coconut activated carbon	509.0	(Lee et al., 2006)
Chitosan	30.4	(Crini & Badot, 2008)
Sewage sludge	115	(Won et al., 2006)
Landfill sludge	159	(Won et al., 2006)
Activated carbon from Brazilianpine fruit shell	472.0	(Calvete et al., 2010)

2.2.1 Dye classification

Dyes had been classified according to the chemical classifications which are synthetic dye and natural dyes. Natural dye is safe because made up from organic material such as vegetable matter, insects or minerals without chemical treatment (El-Khatib et al., 2014). Natural dyes are categories as minimal toxicity and low allergic (Sivakumar et al., 2009). The advance in natural dye application is cheap, renewable resource, non-carcinogenic, biodegradable (Sinha et al., 2012). Natural dye also act as antibacterial with the extraction of *T. catappa* leaves and *A. heterophyllus* leave (Prusty et al., 2010). Most synthetic dye is made up from chemical substance such as mercury, copper, toluene and benzene that harmful to human when chronically exposed on these chemical (Sivakumar et al., 2009). Most the application and demand is toward synthetic dyes due to their long lasting and effectiveness in many sector industries such as textile and cosmetic. Synthetic dye is divided into three categories which are water soluble dye, water insoluble dye and in-situ colour formation. The water soluble dye such as direct dyes, reactive dyes, basic dyes, metal complex dyes, acid dyes and solubilised vat dyes. Vat dyes, disperse dyes and sulphur dye are belong to water insoluble dye. The insitu colour formation usually involves the azoic colour.

2.2.2 Reactive Azo Dye

Reactive Orange 16 is anionic dye that belongs to the reactive azo dye class. Azo dye is water soluble and contains aromatic amine. It is derived from benzidine and carcinogenic which a factor induce the cancer in human (Naidu & Aruna, 2013). Azo dye colour is high durability affect greater resistance to washing (Kiernan, 2014). Azo dyes have pendent side chain for substrate join and a major commercial application involving the attachment to the hydroxyl groups of cellulose.

2.2.3 Factor Affecting Biochar Sorption

i. pH

In anionic, the sorption of adsorbate to adsorbent may decrease due to the electronic repulsion occur between anionic at high pH and highly negative charge on the top substance. In cationic contamination, the sorption increase by rising pH. It force the functional group increased the net negative charge on surface. The different pH of some chemical properties may conduct to the different of sorption mechanism (Tan et al., 2015).

ii. Temperature

The increasing temperature enhances the sorption between adsorbate and molecule and the positive enthalpy change (ΔH) assume as endothermic. The negative Gibbs free energy (ΔG) implied a thermodynamic and spontaneous sorption. When the biochar pyrolyzed under low temperature, Gibbs also in low value due to higher noncarbonized in biochar and the more polar structure to the polar adsorbent

(Aysu & Kucuk, 2015).

iii. Contact time

Contact time is influence to the adsorption process. Standard adsorption between adsorbate molecules and adsorbent need longer time to occupy all the surface site of adsorbent. Adsorption will touch down until it reach equilibrium phase.

iv. Particle size of adsorbent

Adsorption capacity rise with smaller size of adsorbent due to the highs in surface area, charge density, negative charge, and microsporous form on the adsorbent. In this study, the biochar from bamboo is high surface area than raw bamboo because generated biomass from carbonization (Zheng et al., 2010). Small size of adsorbent has limitation on the active site and only few adsorbate can attach to it.

2.3 Adsorption as basis of dye removal

Dyes have features like resistance to heat, climate change and ultraviolet ray. The active and passive transport are main mechanism that needed in adsorption process. The molecules that exposed to the cell surface are tending to attach on the binding site on that cell surface with the chemical affinity. Dye has affinity with various cell surfaces which means the ability of adsorbent to bind with many type of dyes (Rafatullah et al., 2010). Biomass such as bamboo can be as removing agent for dye because is plentifully accessible, have a large portion of the kinds and free mind boggling pretreatment or actuation process.

2.4 Significance of Reactive Orange 16 dye removal

In textile industry, RO16 dye is chromophore which is molecules that responsible for colour of compound and commonly used in cellulose fibers dyeing application. It also applied on cotton, wool and nylon under weakly acid. It also has a low utilization in industry than other dyes because it functional groups that bond to water can cause hydrolysis. RO16 removal is important to preserve ecology and human well being.

2.5 Adsorption isotherm

Adsorption isotherm is fundamentally vital to depict about the interaction between molecule and adsorbents also the way to decide the utilization of adsorbents been archive the optimum phase. It relates association amongst the collection of molecule adsorbate by adsorbent and the balance of particle adsorbate be left in solution (Calvete et al., 2010). Isothermal adsorption is abundance energy because of molecule interaction with surface of adsorbent might be predict to be withdrawn to keep the constant temperature (Ziolkowska, 2016). Adsorption isotherm refer to monolayer adsorbate, has uniform value of adsorption enthalpies and thickly stuffed admolecules force the consideration of interaction energies during adsorption (Keller et al., 2005). Langmuir and Freundlich were selected to analyse the adsorption system. Langmuir model is theoretical construct that predict there is only monolayer on the surface, while the Freundlich isotherm is empirical, does not have restriction.

Langmuir and Freundlich also used in application of chemisorption and physisorption (Balpreet Singh, 2016). Langmuir isotherm predicts that dynamic equilibrium exists amongst adsorbed molecule and free state molecule because adsorption occur in one monolayer and cause permanent adsorbed. Adsorption will reach the saturation state when it overhelms the surface pressure isotherm (Graham &

Phillips, 1979). Adsorption will stop after reach saturation pressure because have limit number of empty space on adsorbent surface. All sites are occupied at high pressure state. Freundlich is empirical be regard as amount of molecule attach the charge site per unit mass of adsorbent along with pressure (Balpreet Singh, 2016). Freundlich also believe that heterogenous surface energies help in surface coverage (Hameed et al., 2007). The factor that causes the energies of bond become lower with surface density is due to a compaction molecule on adsorbent surface sites and enhances the lower interaction between adsorbate and adsorbent. It is because the surface density of adsorbent become increases after adsorption reach the equilibrium phase. The saturation of solid surface cannot be estimate by Freundlich, thus it estimates mathematically of infinite surface coverage on adsorbent (Reed & Matsumoto, 1993).

2.5.1 Type Adsorption

Adsorption process has two types which is physical adsorption and chemical adsorption shown at Figure 2.5. Physical adsorption usually used in adsorption application while chemisorption relies on catalysis (Giannozzi et al., 2003).

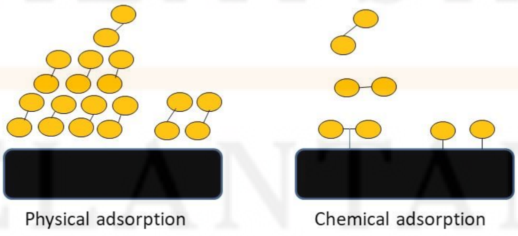


Figure 2.5: Type adsorption

Source: www.emedicalprep.com

Physisorption or known as physical adsorption involves the van der Waals adsorption as attractive or repulsive forces. Van der Waals force consist of dipole-dipole, dipole-induced dipole and London forces. The interaction between adsorbate and adsorbent is weak (Khomyakov et al., 2009). Thus, it does not require any activation energy and induce the increasing pressure. Physical adsorption usually reversible in nature, forms multi-molecular layers and physiosorption of molecule on surface can be more than one layer. It takes place at low temperature that low enthalpy change.

The physisorption can reach the equilibrium rapidly depend on adsorbent and can be used on molecule adsorbed in charcoal. A distinct chemical reaction occurs specially in chemisorption. It is irreversible in nature and has chemical bond forces of attraction. It is highly specific, need activation energy and monomolecular layers. In chemisorption molecule adsorbate perform the covalent chemical reaction to join with the site of adsorbent surface with high heat of adsorption (Berger & Bhown, 2011). The chemisorption can reach the equilibrium slowly and depend on adsorbate and adsorbent.

2.6 Characterisation technique of adsorbent

Characterisation of adsorbent was analysed by two methods to determine its physico-chemical properties. Methods consist of Fourier Transforms Infrared Spectroscopy (FTIR) analysis and Scanning Electron Microscope (SEM) analysis.

CHAPTER 3

MATERIAL AND METHOD

3.1 Materials

The materials that used in this study are bamboo that collected from Pasir Gudang, Johor and Agro Park University Malaysia Kelantan, Jeli. The bamboo needed to carry out carbonization process to form biochar. Reactive Orange 16 dye act as adsorbate. The distilled water was used to prepare all the reagent and solution.

3.2 Apparatus and equipment

The equipment that used in this study are weighing balance, sieving machine, UVVis Spectrophotometer, furnace and blender. The apparatus was used are volumetric flask (500 mL and 1000 mL), beaker (100 mL and 200 mL), measuring cylinder (5 mL, 10 mL and 50 mL), conical flask (250 mL), reagents bottle (100 mL and 1000 mL), cuvette, filter paper, filter funnel, stainless steel sieve (125 µm), spatula and glass rod.

3.3 Chemical and reagents

Chemical that involved in this study is Reactive Orange 16 ($C_2OH_{17}N_3Na_2O_{11}S_3$), hydrochloric acid and sodium hydroxide, potassium chloride, potassium hydrogen phthalate, Potassium dihydrogen phosphate and tris (hydroxymethyl) aminomethane.

3.4 Preparation of adsorbent

The dry and died bamboo was collected from Pasir Gudang, Johor and Agro Park University Malaysia Kelantan, Jeli. The bamboo was cut into small size and the dirt was removed. The bamboo was dried under the sunlight to remove the water content in bamboo. The blended bamboo was sieve into 125 µm. Then the bamboo was put inside the crucible in 8 gram for 400 ℃, 600 ℃ and 800 ℃ respectively for 2 hour. The bamboo had run carbonization process in air atmosphere using furnace. The biochar of bamboo formed was put in a sealed polyethylene bag and stored into desiccator.

3.5 Preparation of adsorbate (Reactive Orange 16 Stock Dye Solution)

0.5 g of dye powder was dissolved in distilled water using 500 mL volumetric flask to prepare stock solution of Reactive Orange 16 with concentration of 1000 mg/L.

3.6 Preparation of calibration curve

Stock solution of Reactive Orange 16 dye was diluted with distilled water using 50 mL volumetric flask at 0.5, 2.0, 4.0, 6.0, 8.0 and 10.0 mg/L. Distilled water was used as blank (0 mg/L). The blank and stock solution was introduced into UV-Vis spectrophotometer at wavelength of 494 nm. Value obtained from absorbance reading was used to construct Reactive Orange 16 calibration curve.

3.7 Optimisation of the adsorption studies

Optimisation of the adsorption studies are the effect of carbonization temperature, effect of adsorbent dosage, effect of initial concentration dye, effect of contact time and effect of pH.

3.7.1 Effect of carbonization temperature

The effect of carbonization temperature was studied at different temperatures which are 400 °C, 600 °C and 800 °C using furnace. Bamboo waste at size of 125 µm was added into 3 crucibles respectively to transform into bamboo biochar.

3.7.2 Effect of adsorbent dosage

Effect of adsorbent dosage was studied at different adsorbent dosages which are 0.5, 1.0, 2.0, 3.0, 4.0, 5.0 g for 24 hours at room temperature. The optimum size that obtained from the previous study was used as control value. The mixture of dye and adsorbent was stirred by using glass rod for a few minutes and leave for 24 hours.

3.7.3 Effect of Initial concentration dye

The effect of initial dye was analysed by using the optimum carbonization temperature and optimum adsorbent dosage from the previous study. The initial Reactive Orange 16 concentration was studied at 50, 100, 150, 200, 250 and 300 mg/L for 24 hour at ambient temperature. The mixture of dye and adsorbent was stirred by using glass rod for a few minutes and leave for 24 hour.

3.7.4 Effect of contact time

The effect of contact time was carried out at 4 h, 8 h, 12 h, 16 h, 20 h and 24 h. The optimum of carbonization temperature, adsorbent dosage and initial concentration dye was used as control value. The sample was filtered using filter paper and the supernatant been analysed using UV-Vis spectrophotometer

3.7.5 Effect of pH

The optimum values of carbonization temperature, adsorbent dosage, initial dye concentration and contact time was used in this study. The buffer solution was prepared at pH 4, 5, 6, 7 and 8. After the adsorption reach equilibrium in different pH, the samples need to filter to record the absorbance reading by UV-Vis spectrophotometer at 494 nm. Table 3.1 shows the buffer solution.

Table 3.1: Buffer solution

pH	COMPONENT
4	100 ml 0.1 M potassium hydrogen phthalate + 0.2 ml of 0.1 M HCl
5	100 ml 0.1 M potassium hydrogen phthalate + 45.2 ml of 0.1 M NaOH
6	100 ml 0.1 M KH_2PO_4 + 11.2 ml of 0.1 M NaOH
7	100 ml 0.1 M KH_2PO_4 + 58.2 ml of 0.1 M NaOH
8	100 ml 0.1 M tris (hydroxymethyl) aminomethane + 58.4 ml of 0.1 M HCl

Source: Dhanlal (2000)

3.8 Characterization Technique of Adsorbent

In this study, 3 samples such as raw bamboo, biochar bamboo, (BB) and biochar bamboo, (BB) adsorbed by RO16 dye was analysed using Fourier transform infrared, FTIR and Scanning Electron Microscope, SEM. FTIR equipment was used to identify the element and functional group in samples. The SEM equipment was used to describe the surface and the porosity of samples.

3.9 Data Analysis

In this study, data was analysed by using t-test and adsorption isotherm.

3.9.1 T-test

Standard deviation was calculated using equation.

$$s^2 = \frac{(n_1-1)s_1^2+(n_2-1)s_2^2}{(n_1+n_2)-2} \tag{3.1}$$

Where:

n_1 = total number of measurements in first set

n_2 = total number measurement in second set s_1

= standard deviation of first set

s_2 = standard deviation of second set

Pooled estimate standard deviation, was calculated using equation.

$$s = \sqrt{s^2} \tag{3.2}$$

T-test was calculated using equation:

$$t = \frac{x_1 - x_2}{s \times \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \tag{3.3}$$

Where:

$\bar{x}_1$ = mean of first set $\bar{x}_2$ = mean of second

set n_1 = total number measurement in first

set n_2 = total number measurement in set

two

3.9.2 Adsorption capacity

Adsorption capacity was evaluated using equation,

$$q_e = \frac{(C_o - C_e)\,V}{m} \qquad (3.4)$$

Where:

C_e = Equilibrium dye concentration in the solution (mg/L)

C_o = Initial dye concentration in the solution (mg/L)

V = Volume of solution (L) m

= Mass of adsorbent (g)

3.9.3 Langmuir adsorption model

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \qquad (3.5)$$

q_e is dye uptake (mg/g) while q_{max} is maximum dye uptake (mg/g) in constant

Langmuir equilibrium, K_L with equilibrium concentration, C_e.

i. Linearised Langmuir isotherm

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\ K_L} + \frac{1}{q_{max}} C_e \tag{3.6}$$

Where, q_e is amounts if dye adsorbed at equilibrium (mg g^{-1}), and C_e is amounts of unadsorbed dye concentration in aqueous solution (mg L^{-1}), q_{max} is the monolayer biosorption capacity of the adsorbent (mg g^{-1}). K_L is the Langmuir adsorption constant (L mg^{-1}) and related to the free energy of adsorption (Malviya et al., 2017).

3.9.4 Freundlich adsorption model

$$Q_e = K_f\, C_e^{\frac{1}{n}} \tag{3.7}$$

Where:

K_f = Freundlich isotherm constant (mg/g) n

= adsorption intensity

C_e = the equilibrium concentration of adsorbate (mg/L)

Q_e = the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

i. Linearised Freundlich isotherm

$$\log Q_e = \frac{1}{n} \log C_e + \log K_f \tag{3.8}$$

Where:

K_f = constant value which related to adsorption capacity (mg/g)

1/n = Empirical parameter related to the adsorption intensity which depends on heterogeneity.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of Adsorbent

In this study, the bamboo biochar used as adsorbent for removal of Reactive Orange 16 dye. The adsorbent was characterized using Scanning Electron Microscope (SEM) and Fourier transform infrared (FTIR) spectra.

4.1.1 Scanning Electron Microscope, SEM

Figure 4.1 was shows the SEM images of raw bamboo in magnification x 1000. Raw bamboo structure arranged with ground tissues such as parenchyma cells and also vascular bundles such as metaxylem vessels and fibers (Yu et al., 2014). Figure 4.2 was shows the SEM images of bamboo biochar,BB in magnification x 1000. BB had undergone combustion through carbonization by using furnace. Conversion from raw bamboo to the biochar increasing the porous development, surface area and carbon content (Beesley et al., 2011). Figure 4.3 was shows the SEM images of BB adsorbed with RO16 in magnification x 1000. The porous of BB had fully occupied with Reactive Orange 16 dye. The adsorption process occurred with existing electrostatic attraction between anionic dyes with surface site of adsorbent (Arami et al., 2005). SEM result shows the BB has high porous while raw bamboo has less porous.

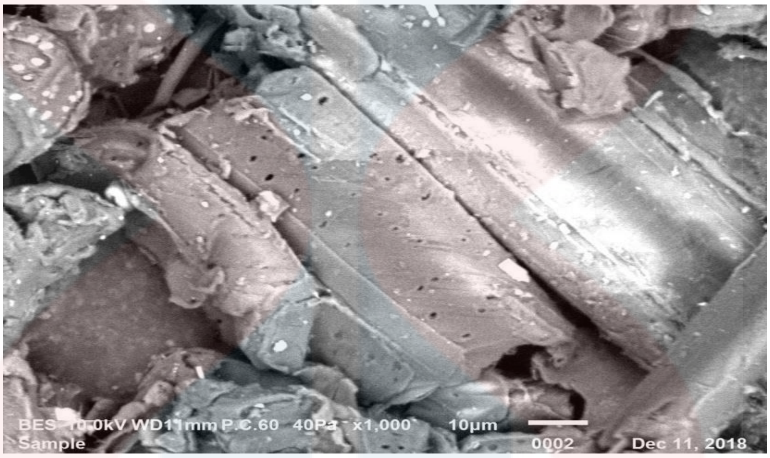


Figure 4.1: SEM images of raw bamboo (magnification = 1000)

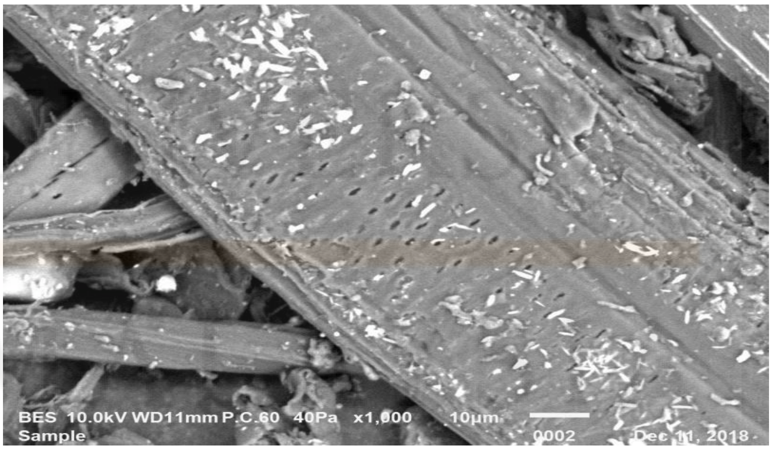


Figure 4.2: SEM images of biochar bamboo, BB (magnification = 1000)

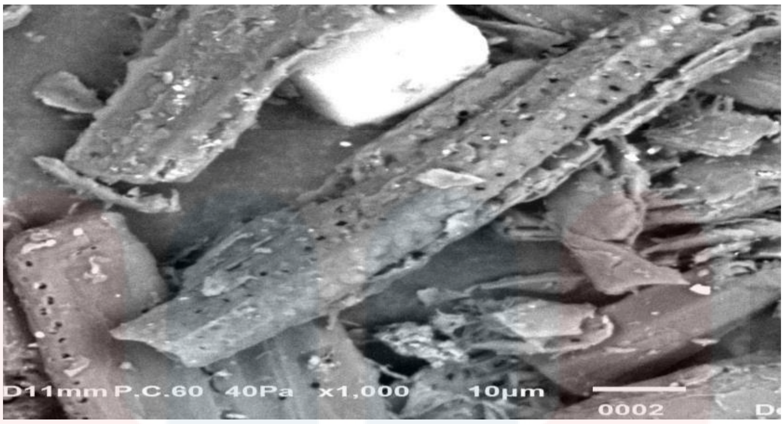


Figure 4.3: SEM images of biochar bamboo,BB adsorbed with RO16 (magnification = 1000)

4.1.2 Fourier transform infrared, FTIR

The FTIR spectrum on raw bamboo, BB and BB adsorbed by RO16 dye was shown in Figure 4.4. According to Guo et al., (2014), elemental that confirms in surface of bamboo was carboxyl groups. However, the functional group was identified in raw bamboo were inorganic phosphates, alkynes monosubstituted and aliphatic hydrocarbon. Inorganic phosphate has two strong bands at wavelength 550-1000 cm^{-1}. The mono-substituted acetylenes can easily be identified by the strong −C:::C−H (carbon hydrogen) stretching absorption around 3300 cm^{-1}. Aliphatic groups vibrational modes are the C−H stretching around 3000 cm^{-1} and the −CH deformation modes around 1460 cm^{-1} and 1380 cm^{-1}.

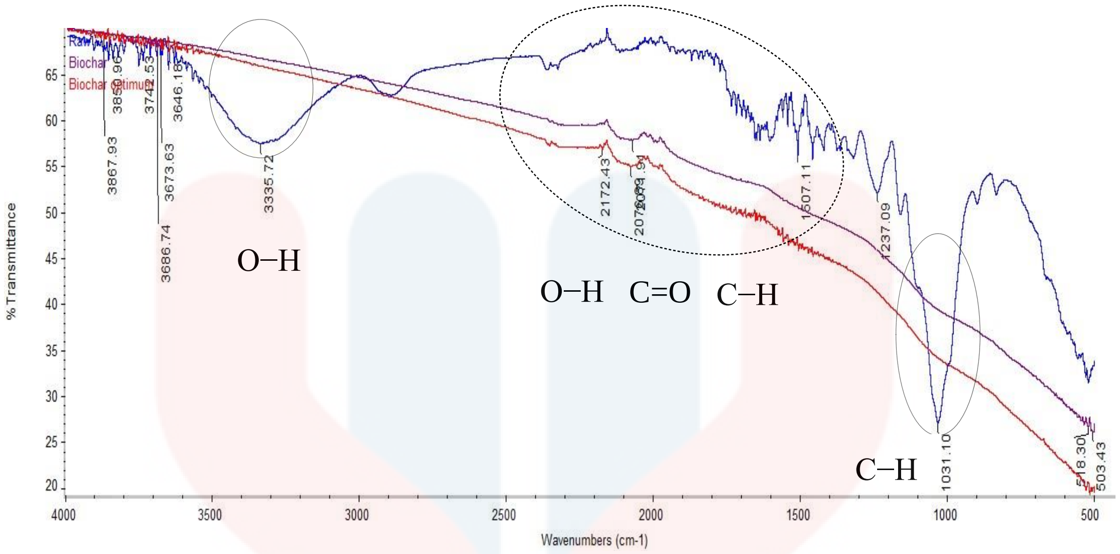


Figure 4.4: FTIR on raw bamboo (—) and BB (—) and BB adsorbed by RO16 dye (—)

Based on the spectrum, the peak at BB and BB adsorbed by RO16 dye is quite similar but different peak for raw bamboo at 3335.72 cm^{-1}. The spectrum shows linear peak at BB and BB adsorbed by RO16 dye while high peak for raw bamboo. According to Bykov (2008), the band near 3000–3500 cm^{-1} indicates the presence of hydroxyl groups of cellulose and lignin in raw bamboo. OH stretching at band 3200–3500 cm^{-1} and aliphatic CH stretching at band 2820–2980 cm^{-1} was loss when expose to heat. According to Antal & Gronli (2003), the formation of unsaturated C−C bonds and carbonyl groups, caused by the elimination of water effect from the carbonization process. Thermal effect influence carbonyl groups and substitution in aromatic rings (Angin, 2014).

According to Angin (2014), band 1985−2462 cm^{-1} represent aliphatic band (C−H). The raw bamboo display highest frequency of peak at 1500−2000 cm^{-1} followed by BB adsorbed by RO16 dye and BB. Hydrogen and OH group might extract from aromatic ring during heat treatment at slow temperature and adsorption in acidic solution. The raw bamboo shows the highest peak because had stored in oven at 50 °C during drying step before carbonization. Thus the elements inside raw bamboo keep remain. BB adsorbed by RO16 show a few vibrations compared to BB due to effect of adsorption at optimum pH 6 which is acidic. The acidic solution contains H with positive charge as contributor for peak formed. The functional group in BB is inorganic

nitrate. There are three bands in BB such as 1780 cm^{-1}, 1380 cm^{-1} and 830 cm^{-1}. The 1780 cm^{-1} medium band has C=O stretching and carboxyl compound. The 1380 cm^{-1} strong band has =OH, CH bending consists of hydrocarbon, acid, phenol, olefin and alcohol compound. The 830 cm^{-1} is weak band has =C−H functional group and consist of aromatic hydrogen compound (Li et al., 2014). However, the BB shows linear peak due to high temperature causes some element loss to surround.

Based on the spectrum only raw bamboo shows high peak while BB and BB adsorbed by RO16 shows linear peak at 1031.10 cm^{-1}. In raw bamboo, band 1030 cm^{-1} caused by primary alcoholic and methoxyl group. It represent O-H deformation or C−O stretching band (Hergert, 1960). However, the peak of BB and BB adsorbed by RO16 shows the linear peak because of elements loss during carbonization process.

4.2 Calibration curve

Figure 4.5 shows the calibration plot of RO16 at 494 nm and a linear graph was obtained between concentration dye and absorbance reading. The coefficient value obtained from calibration curve indicated the good result which is 0.9933. Correlation coefficient (R^2) as a bench mark to measure the acceptability of studies that indicate 1 or near to 1 as precise correlation. The liner calibration equation was used to obtain the final concentration of dye after adsorption

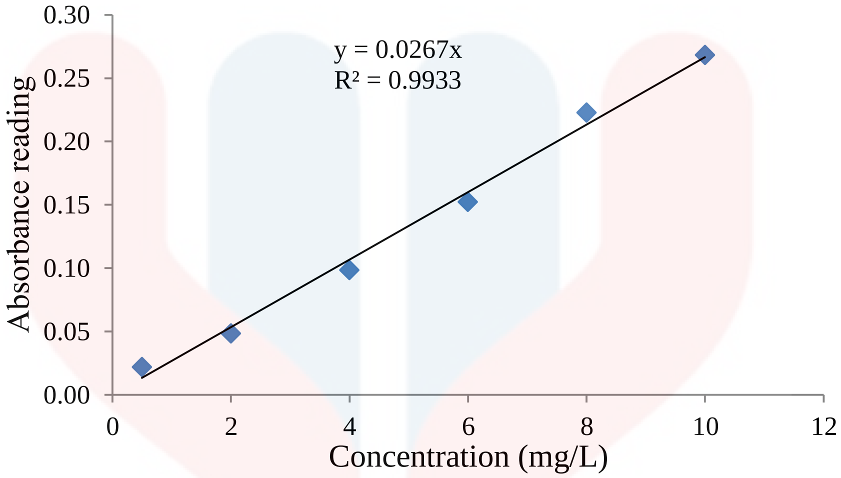


Figure 4.5: Linear calibration curve of RO16 at 494 nm

4.3 Effect of carbonization temperature

In this study, the bamboo was exposed to the heat for 2 hour at different temperature 400 °C, 600 °C, and 800 °C inside the furnace. The effect of carbonization temperature on removal of RO16 dye was shown at Figure 4.6.

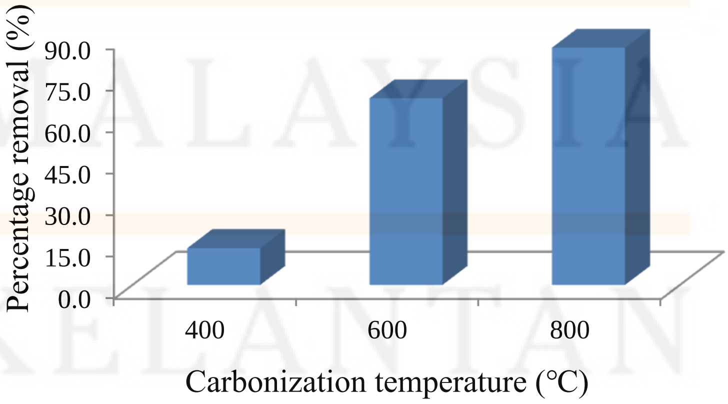


Figure 4.6: Effect of carbonization temperature on removal of RO16. Condition: adsorbent dosage of 1 g; adsorbent size of 125 µm; dye concentration of 50 mg/L; solution volume of 100 mL; room temperature; 24 hour.

The optimum carbonization temperature was 800 ℃ because gave the highest percentage removal, 85.5 %. The biochar yield slightly decrease from 400 ℃ to 800 ℃ due to higher loss of volatile matter and the emission of H_2O, CO_2, CO, CH_4, and H_2 at high temperature (Antal & Gronli, 2003). According to Ahmad et al., (2013), carbonization temperature influenced the pore structure and surface area of biochar due to enrichment of the micropore volume after volatile materials emitted. Furthermore high carbonization temperature produces high in carbon content, high aromatic structures and low polarity. It increases the efficiency of adsorption capacity on removal of RO16 dye. T-test result of carbonization temperature was shown in Table 4.1. Carbonization temperature, 800 ℃ have significant difference with 400 ℃ and 600 ℃. However, 800 ℃ had chosen as the optimum because has the lowest average on OD reading (Abs) using UV-Vis spectrophotometer (see Appendix B: Table B1).

Table 4.1: T-test result for effect of carbonization temperature (℃)

Carbonization temperature ℃	**Value of t-test (t_6=2.447)**	**Notes**
800 ℃ & 400 ℃	373.739	Have significant difference
800 ℃ & 600 ℃	82.941	Have significant difference

4.4 Effect of adsorbent dosage

The effect of adsorbent dosage on removal of RO16 dye was shown in Figure 4.7. The variety of BB dosage such as 0.5 g, 1 g, 2 g, 3 g, 4 g and 5 g were investigated.

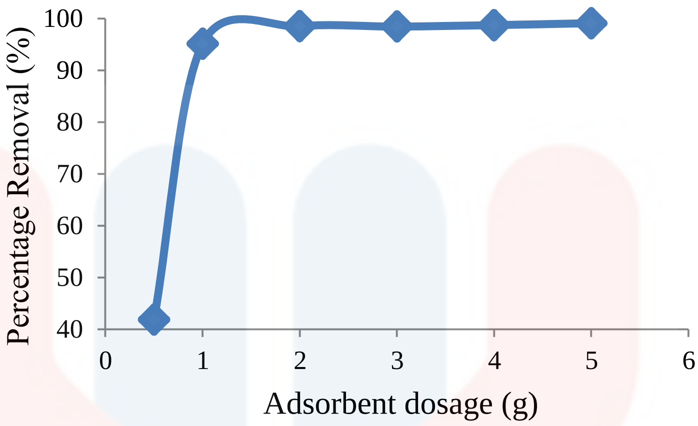


Figure 4.7: Effect of adsorbent dosage on removal of RO16 dye using bamboo biochar. condition: adsorbent size of 125 µm; dye concentration of 50 mg/L; solution volume of 100 mL; room temperature; 24 hour contact time.

The percentage removal of RO16 dye was slightly increases from 41.873 % to 98.502 % at 0.5 g to 2 g of adsorbent. However the percentage removal remains unchanged at 2 g until 5 g. It regarding the fixed mass of bamboo biochar to adsorb only certain quantity of dye molecule and depends on vacancy of surface site (Guo et al., 2014). Hence high adsorbent dosage helps increasing the percentage removal but remain constant after optimum point. It can be clearly stated from t-test result whereby, there is no significance different after 2 g of adsorbent dosage. In high dosage, dye molecules that adsorb was unfulfilled space of surface site at equilibrium state (Foo & Hameed, 2010). It is because of limitation of dye concentration in high dosage. In this study, the optimum value is at 2 g adsorbent dosage in 100 mg/L dye concentration and 100 mL of solution volume. Table 4.2 shows the t-test result for effect of adsorbent dosage. 2 g of adsorbent dosage have no significant different with other dosage. However, 2 g had chosen as optimum because it became colourless and was firstly appeared at this dosage.

Table 4.2: T-test result for effect of adsorbent dosage (g)

Adsorbent dosage (g)	Value of t-test (t_6=2.447)	Notes
2 g & 1 g	0	No significant difference
2 g & 3 g	0.579	No significant difference
2 g & 4 g	0	No significant difference

4.5 Effect of initial concentration dye

The different initial dye concentration for removal of RO16 dye was shown in Figure 4.8 while the data was shown in Appendix B (Table B3).

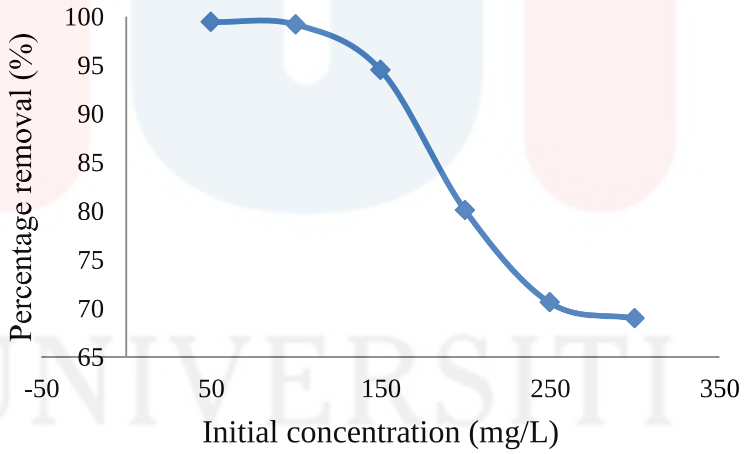


Figure 4.8: Effect of initial dye concentration on removal of RO16 dye using biochar bamboo. Condition: adsorbent dosage of 2 g; adsorbent size of 125 µm; solution volume of 100 mL; room temperature; 24 hour contact time.

Initial adsorption was rapid because having strong driving force between liquid and adsorbent. Then, become slow affect from loading surface. Based on the graph, 50 mg/L and 100 mg/L have high percentage removal 99.438 % and 99.176 % respectively and slow down at above 100 mg/L concentration. In this study 100 mg/L was chosen as the best optimum initial dye concentration. It is because 2 g of optimum adsorbent dosage has ability to adsorb high initial concentration dye rather than low initial concentration dye. It is also having higher maximum adsorption capacity, q_{max} (mg/g) at equilibrium compared to 50 mg/L (see Appendix B: Table B3). Adsorption capacity for 100 mg/L is 4.959 mg/g while 50 mg/L is 2.486 mg/g. The percentage removal slightly decreases from 94.519 % to 68.958 % at 150 mg/L to 300 mg/L due to high

concentration dye but limitation of adsorbent dosage.

The final dye concentration also increases due to saturated adsorption at equilibrium phase. The dye molecules are free because unable to adsorb by adsorbent. According to Hameed & El-Khaiary (2008), the constant slope from 50 mg/L to 100 mg/L indicates that the thickness of external boundary layer which means high resistance to mass transfer. However, the slope become decrease at 150 mg/L until 300 mg/L due to the less resistance to mass transfer in the external boundary layer. The t-test result for effect of initial dye concentration was shown in Table 4.3. Initial dye concentrations, 100 mg/L have no significant difference with 50 mg/L. The clearance colour for both dye concentration also not show the different. 2 g of adsorbent dosage are most effective for treating high dye concentration such as 100 mg/L.

Table 4.3: T-test result for effect of initial dye concentration (mg/L)

Initial dye concentration (mg/L)	**Value of t-test (t_6=2.447)**	**Notes**
100 mg/L & 50 mg/L	1.140	No significant difference
100 mg/L & 150 mg/L	23.039	Have significant difference
100 mg/L & 200 mg/L	124.038	Have significant difference

4.6 Effect of contact time

The effect of contact time for removal of RO16 dye was shown in Figure 4.9. The data was shown in Appendix B (Table B4). The variety of contact time such as 4 h, 8 h, 12 h, 16 h, 20 h and 24 h was studied in this study.

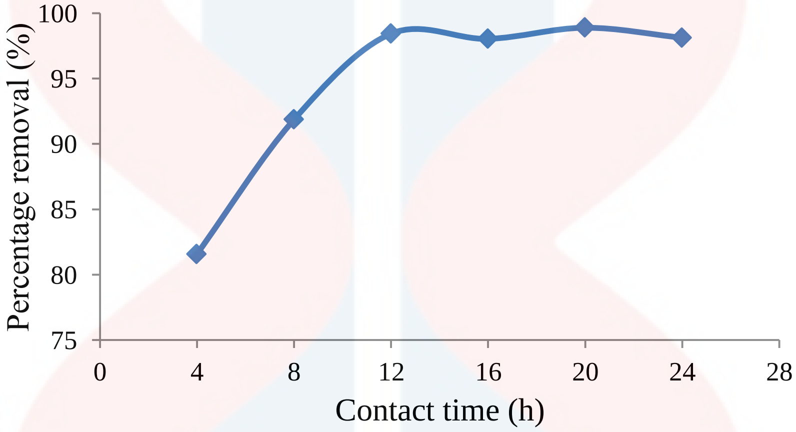


Figure 4.9: Effect of contact time on removal of RO16 dye using biochar bamboo. Condition: adsorbent dosage of 2 g; initial dye concentration of 100 mg/L; adsorbent size of 125 µm; solution volume of 100 mL; room temperature.

In this study, 12 hour was chosen as optimum contact time because of the highest percentage on removal of RO16 dye, 98.45 %. The percentage removal increase at 4 hour to 12 hour and remain constant with increasing contact time. However percentage removal at 6 h decrease due to the repulsion occurs during stabilizing at equilibrium point. This is affect from attractive forces such as van der Waals forces and electrostatic attractions force that occurs between the dye molecule and the adsorbent. The diffusion started from external surface of bamboo biochar to the pore diffusion into the intraparticle matrix bamboo biochar until it reach equilibrium phase (Mahmoud et al., 2012). T-test result for effect of contact time (h) was shown at Table 4.4. Effect of contact time at 12 h has no significant difference with 20 h and has significant difference with 8 h and 16 h.

After adsorption, solutions become colourless at 12 h, 16 h, 20 h and 24 h. However, 12 h have ability to treat dye effectively in a shortest time.

Table 4.4: T-test result for effect of contact time (h)

Contact time (h)	**Value of t-test (t_6=2.447)**	**Notes**
12 h & 8 h	43.718	Have significant difference
12 h & 16 h	2.505	Have significant difference
12 h & 20 h	2.035	No significant difference

4.7 Effect of pH

Figure 4.10 shows the effect of pH against percentage removal of RO16 dye using biochar bamboo (BB). The percentage dye removal was examined in different phase of pH such as acidic, neutral and alkali at pH 4, 5, 6, 7, 8. pH 6 was chosen as optimum value because has the highest percentage removal, 99.94 %. pH condition is important in adsorption because influence the surface charge of adsorbent, dissociation of functional groups on the active sites of the adsorbent and the structure of the dye molecule. Bamboo has carboxyl group. However, the carboxyl group is positive charged under acidic condition (Khan, 2018). Reactive Orange 16 is anionic dye. Therefore, high electrostatic attraction occurred between the positive charge on adsorbent and negative charge on RO16 dye in adsorption process.

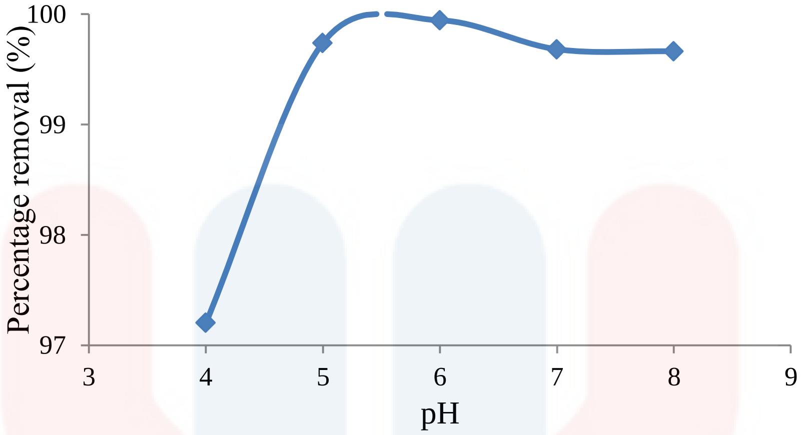


Figure 4.10: Effect of pH on removal of RO16 dye using biochar bamboo. Condition: adsorbent dosage of 2 g; adsorbent size of 125 µm; dye concentration of 100 mg/L; solution volume of 100 mL; room temperature; 12 hour contact time.

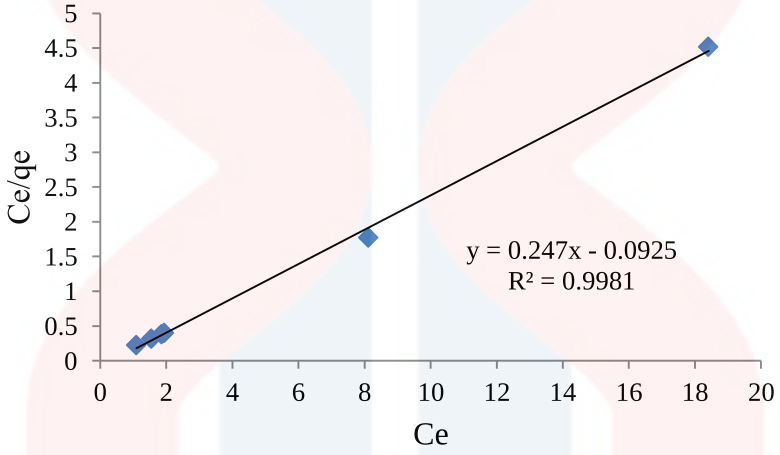
The percentage removal in pH 7 and pH 8 is less than pH 6. According to Yang et al., (2014), the biochar become less positively charged at high pH like 7 and 8. It forces an excess OH^- ion to compete with the anionic groups of dye for bind to the surface site of adsorbent. Therefore, the percentage removal and adsorption capacity of bamboo biochar at high pH was significantly lower than low pH. However, the percentage removal of RO16 at pH 4 is lowest due too many negative charges on solution from dye and buffer solution and reduces the adsorption efficiency. The t-test result for effect of pH was shown in Table 4.5. pH 6 has no significant difference between pH 5, 7 and 8 and formed same clear colour. pH 6 is the optimum due to have high percentage removal of RO16.

Table 4.5: T-test result for effect of pH

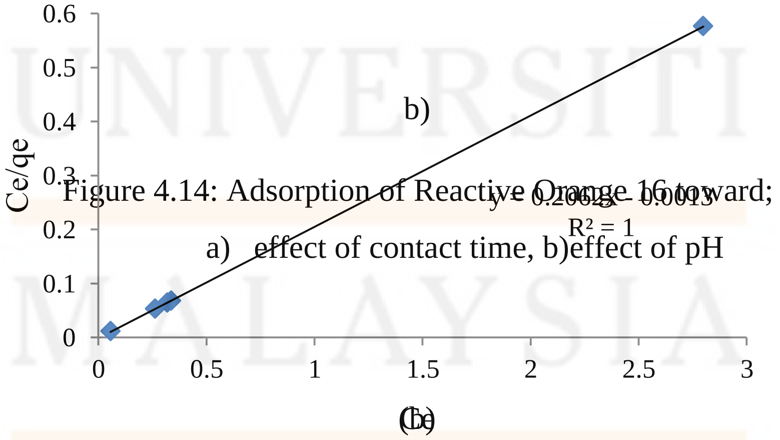
pH	**Value of t-test (t_6=2.447)**	**Notes**
6 & 5	1.874	No significant difference
6 & 7	1.982	No significant difference
6 & 8	1.856	No significant difference

4.8 Adsorption Isotherm

Figure 4.11 and Figure 12 shows the effect of contact time (a) and effect of pH (b) for Langmuir isotherm and Freundlich respectively.



(a)



b)

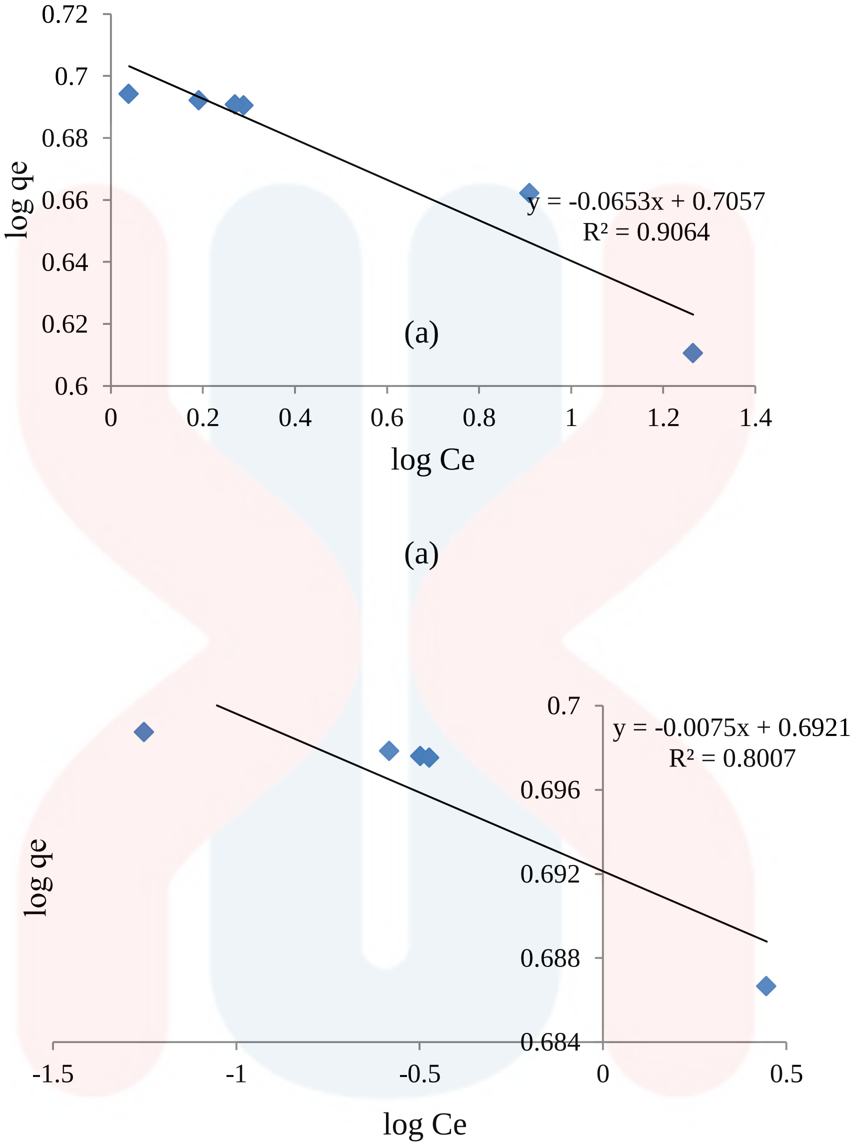
Figure 4.14: Adsorption of Reactive Orange 16 toward;

a) effect of contact time, b)effect of pH

(b)

(b)

Figure 4.11: Langmuir adsorption isotherm for effect of contact time (a) and effect of pH (b).



(a)

(b)

Figure 4.12: Freundlich adsorption isotherm for effect of contact time (a) and effect of pH (b).

Langmuir adsorption and Freundlich adsorption graph was plotted based on data of contact time and data of pH. Parameter of Langmuir isotherm and Freundlich isotherm for RO16 was shown in Table 4.6. The Langmuir isotherm shows the correlation coefficient (R^2) for contact time is 0.998 and pH is 1. Correlation coefficient

(R^2) for pH parameter show the most optimum value because achieve to 1. The Freundlich adsorption shows the correlation coefficient (R^2) for contact time is 0.906 and pH is 0.801. It indicates the Langmuir isotherm is most suitable for adsorption model that used in this study due to nearest to 1. In this study the maximum of dye uptake for bamboo biochar is 4.850 mg/g. The correlation coefficient (R^2) for Freundlich isotherm in pH parameter was not near to 1. It indicates the Freundlich isotherm is not suitable for adsorption model that used in this study. The 4.926 mg/g was constant value for pH which related to adsorption capacity (mg/g). The adsorption capacity depends on different type of agriculture waste as shown in Table 4.7. The value of adsorption capacity on biochar bamboo for these studies was acceptable among the other adsorbent.

Table 4.6: Parameters of Langmuir and Freundlich adsorption for RO16

Adsorption Isotherm	**Parameters**	**q_{max} (mg/g)**	**K_L (L/mg)**	**R^2**
Langmuir	Contact time (h)	4.049	-2.670	0.998
	pH	4.850	-158.614	1
Adsorption Isotherm	**Parameters**	**N**	**K_F (L/mg)**	**R^2**
Freundlich	Contact time (h)	-15.314	5.078	0.906
	pH	-133.333	4.926	0.801

Table 4.7: Adsorption capacity, mg/g at different agriculture waste

Biochar	**Dye**	**Adsorption capacity, mg/g**	**References**
Bael sheel	Patent Blue	3.7	Roy et al. (2018)
Bottom ash	Conggo Red	24.36	Saleh et al.(2012)

Sewage sludge	Methylene Blue	16.21	Fan et al. (2017)
Palm bark	Methylene Blue	2.66	Sun et al. (2013)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, bamboo biochar (BB) has ability to remove Reactive Orange 16 (RO16) dye. The application of bamboo biochar as adsorbent had proven as a good adsorption agent because has high in adsorption capacity and high percentage removal of RO16 dye. In this study, the carbonization concept applied help in forming high porous, high surface area and rich carbon content. It helps in electrostatic interaction between adsorbent and adsorbate.

In this study, the optimum adsorption was identified through different parameter. In effect of carbonization temperature, 800 °C was selected as optimum due to the high percentage removal of RO16 dye. The finding shows the optimum dosage is 2 g; optimum initial dye concentration is 100 mg/L; optimum contact time is 12 hour and the optimum pH is pH 6. In FTIR analysis, some element on bamboo biochar was loss affect from expose to high thermal. The high volume of porous and vascular bundle had proven in

SEM analysis. In this study, the equilibrium data was best fitted to Langmuir isotherm model, suggested the monolayer adsorption between bamboo biochar

(adsorbent) and RO16 dye (adsorbate).

5.2 Recommendation

Recommendation is important to improve or enhance some new knowledge in any case including experiment. Here are some recommendations for this study. First is study the FTIR analysis on biochar bamboo at 400 ℃, 600 ℃ and 800 ℃ for comparison of carbon content. Second is adding some analysis studies such as Brunauer-Emmett-Teller (BET), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) and Response Surface Methodology (RSM) and Thermogravimetric Analysis (TGA).

BET analysis is involved nitrogen multilayer adsorption can used to determine the total surface area, pore volume and pore size distribution of bamboo biochar, BB. The properties of adsorbent can identify through XRD analysis while chemical composition can identify by XRF analysis (Feng et al., 2004). RSM is another statistical method used to evaluate the parameters. TGA is process under thermal condition to determine the weight loss to remove impurities and water dehydration on adsorbent (Banerjee et al., 2017).

Next is adding some parameter such as effect of temperature on solution pH versus time, effect of centrifuge versus filter paper to study different separation technique, effect of moisture on adsorbent to study about the vacancy of active site and effect of stirring rate. All the adsorbent need to put in desiccator because it will affect the element in FTIR and SEM regarding fulfill porous by water molecule and affect unclear image. These studies can apply on the real waste water sample. However other treatment also can be applied to increase the efficiency of adsorbent for dye removal such as the application of activated carbon or modified bamboo by treated with chemical method (Li et al., 2014).

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APPENDIX A

Figure A1: Bamboo steam

Figure A2: Bamboo powder

Figure A3: Biochar from bamboo

Figure A4: Reactive Orange 16 dye change to colourless at optimum condition

Figure A5: Adsorption process

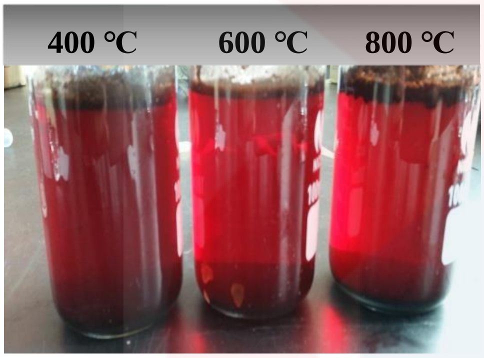

Figure A6: Adsorption on effect of carbonization temperature

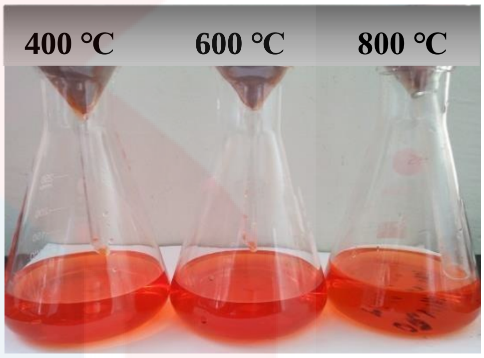

Figure A7: After adsorption on effect of carbonization temperature

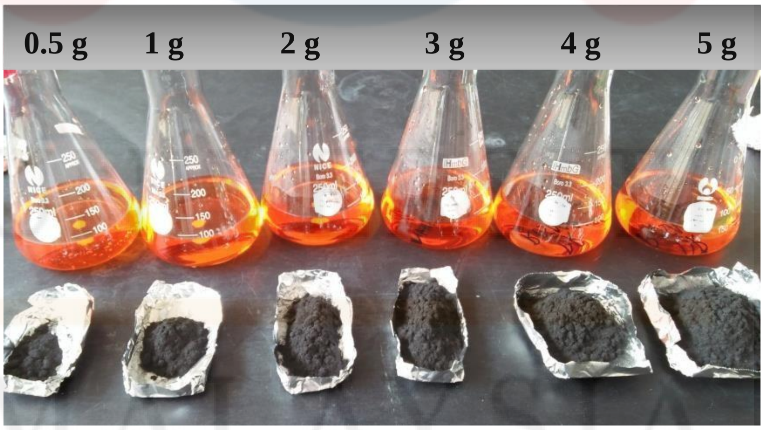

Figure A8: Before adsorption on effect of adsorbent dosage

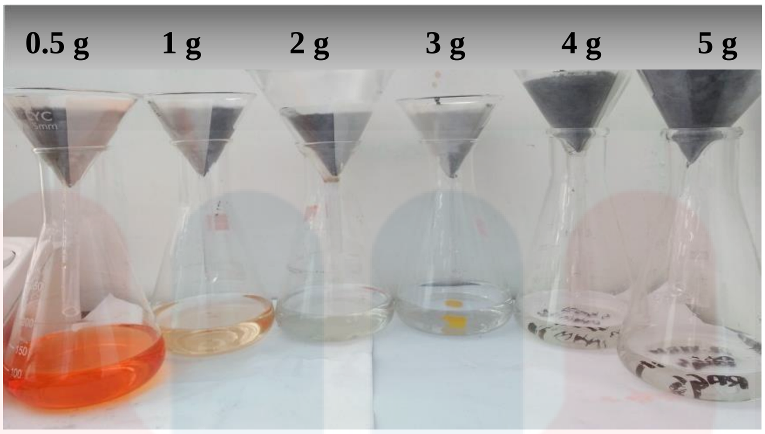

Figure A9: After adsorption on effect of adsorbent dosage

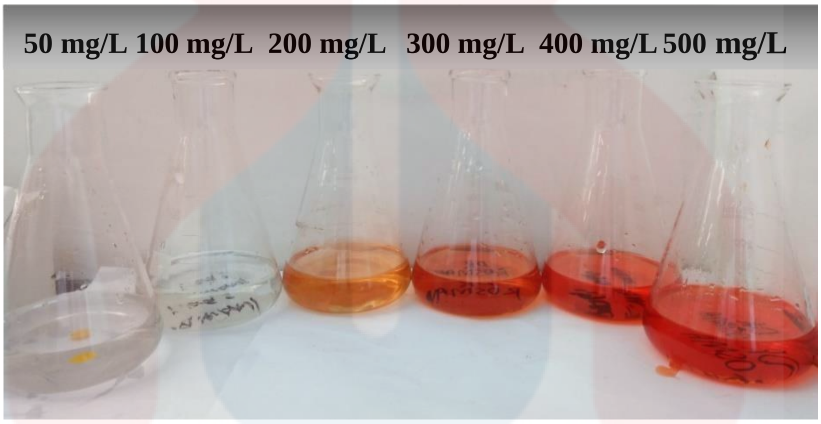

Figure A10: After adsorption on effect of initial dye concentration

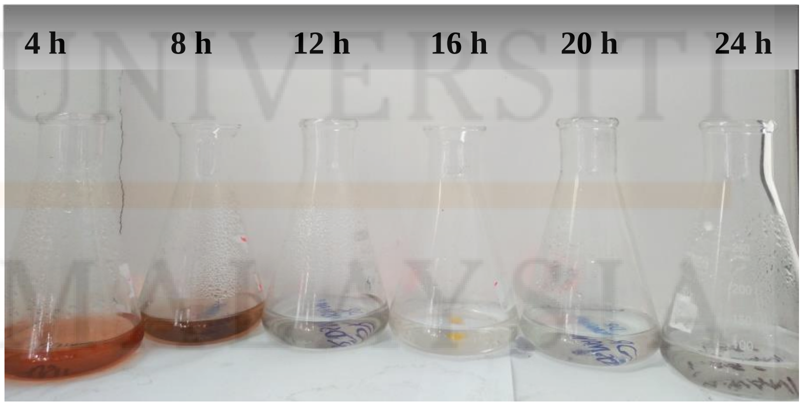

Figure A11: After adsorption on effect of contact time

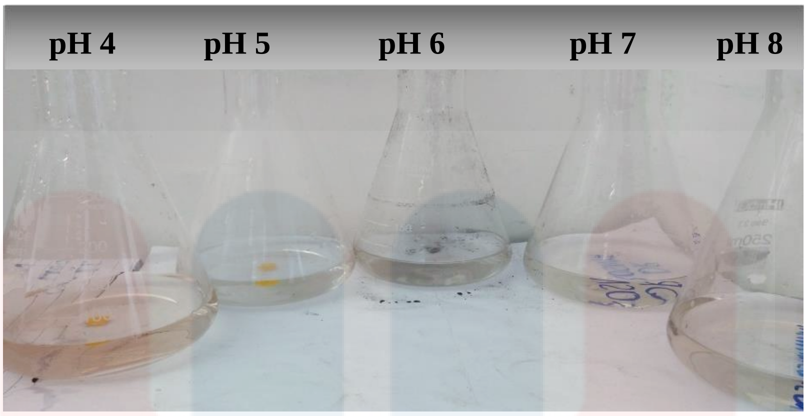

Figure A12: After adsorption of pH

APPENDIX B

Table B1: Effect of carbonization temperature

Carbonization Temperature (°C)	Average on OD Reading (Abs)	Final Concentration (mg/L)	Percentage Removal (%)	Adsorption Capacity (mg/g)
400	1.158	43.380	13.2	0.662
600	0.436	16.339	67.3	3.366
800	0.193	7.219	85.6	4.278

Table B2: Effect of adsorbent dosage

Adsorbent dosage (g)	Average OD on Reading (Abs)	Final Concentration (mg/L)	Percentage Removal (%)	Adsorption Capacity (mg/g)
0.5	0.776	29.064	41.873	4.187
1	0.065	2.434	95.131	4.757
2	0.020	0.749	98.502	2.463
3	0.021	0.777	98.446	1.641
4	0.017	0.637	98.727	1.234
5	0.012	0.449	99.101	0.991

Table B3: Effect of initial concentration

Initial Concentration (mg/L)	Average OD on Reading (Abs)	Final Concentration (mg/L)	Percentage Removal (%)	Adsorption Capacity (mg/g)
50	0.007	0.281	99.438	2.486
100	0.022	0.824	99.176	4.959
150	0.220	8.221	94.519	7.089
200	1.064	39.851	80.075	8.007
250	1.963	73.530	70.588	8.824
300	2.487	93.127	68.958	10.344

Table B4: Effect of contact time

Contact time (h)	Average on OD Reading (Abs)	Final Concentration (mg/L)	Percentage Removal (%)	Adsorption Capacity (mg/g)
4	0.492	18.418	81.583	4.079
8	0.217	8.127	91.873	4.594
12	0.0415	1.554	98.446	4.922
16	0.052	1.948	98.052	4.903
20	0.029	1.096	98.904	4.945
24	0.050	1.863	98.137	4.907

Table B5: Effect of pH

pH	Average on OD Reading (Abs)	Final Concentration (mg/L)	Percentage Removal (%)	Adsorption Capacity (mg/g)
4	0.075	2.800	97.200	4.860
5	0.007	0.262	99.738	4.987
6	0.002	0.056	99.944	4.997
7	0.009	0.318	99.682	4.984
8	0.009	0.337	99.663	4.983

APPENDIX C

Table C1: T-test result of effect of carbonization temperature (℃)

Temperature (℃)	**SD**	**µ**	**S^2**	**S**	**$t_{calc.}$**	**t-test value ($t_6 = 2.447$)**
800 ℃ & 400 ℃	0.001	72.329	0.075	0.274	373.739	HSD
800 ℃ & 600 ℃	0.002	18.234	0.096	0.310	82.941	HSD

Table C2: T-test result of effect of adsorbent dosage (g)

Adsorbent dosage (g)	**SD**	**µ**	**S^2**	**S**	**$t_{calc.}$**	**t-test value ($t_6 = 2.447$)**
2 g & 1 g	0.000	3.367	0.000	0.000	0.000	NSD
2 g & 3 g	0.001	0.056	0.019	0.137	0.579	NSD
2 g & 4 g	0.000	0.225	0.000	0.000	0.000	NSD

Table C3: T-test result of effect of initial concentration dye (mg/L)

Initial concentration dye (mg/L)	**SD**	**µ**	**S^2**	**S**	**$t_{calc.}$**	**t-test value ($t_6 = 2.447$)**

100 mg/L & 50 mg/L	0.002	0.262	0.106	0.325	1.140	NSD
100 mg/L & 150 mg/L	0.004	4.657	0.082	0.286	23.039	HSD
100 mg/L & 200 mg/L	0.001	19.101	0.047	0.218	124.038	HSD

Table C4: T-test result of effect of contact time (h)

Contact time (h)	**SD**	**μ**	**S^2**	**S**	**$t_{calc.}$**	**t-test value ($t_6 = 2.447$)**
12 h & 8 h	0.001	6.573	0.045	0.212	43.718	HSD
12 h & 16 h	0.002	0.393	0.049	0.222	2.505	HSD
12 h & 20 h	0.004	0.459	0.102	0.319	2.035	NSD

Table C5: T-test result of effect of pH

pH	**SD**	**μ**	**S^2**	**S**	**$t_{calc.}$**	**t-test value ($t_6 = 2.447$)**
6 & 5	0.000	0.206	0.024	0.155	1.874	NSD
6 & 7	0.001	0.262	0.035	0.187	1.982	NSD
6 & 8	0.001	0.281	0.046	0.214	1.856	NSD

APPENDIX D

Table D1: Isotherm parameter for adsorption R016

Adsorption Parameter	Isotherm Model	Isotherm Parameter	Value
Contact time	Langmuir	K_L (L/mg) q_{max} (mg/g) R^2	-2.670 4.049 0.998
	Freundlich	KF (mg/g) n R^2	5.078 -15.314 0.906
pH	Langmuir	K_L (L/mg) q_{max} (mg/g) R^2	-158.614 4.850 1.000
	Freundlich	KF (mg/g) n R^2	4.922 -133.333 0.801